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Atomic and Electronic Structures of Zr Atomic Chains *

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The atomic, binding and electronic structures of very thin Zr chains are studied by the first-principles density-functional method. The present calculations reveal that zirconium can form planar chains in zigzag, dimer and ladder structures. The zigzag geometry has two minima. The most stable geometry is the zigzag one with a unit cell rather close to equilateral triangles with four nearest neighbours. The other stable zigzag structure has a wide bond angle and allows for two nearest neighbours. An intermediary structure has the ladder geometry and is formed by two strands. The dimer structure is also found to be more stable than the truly linear chain. All these planar geometries are more favourable energetically than the linear chain. We also show that by going from Zr bulk to a Zr chain, the characters of bonding do not change significantly.

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In the past decade, there has been tremendous interest in low-dimensional nanoscale systems from both the fundamental low-dimensional physics and technological applications, such as in nanoelectronic devices.[1] Nanoscale metallic wires with well-defined structures and usable length have been fabricated.[2−6] A great achievement in nanoscience is the fabrication of stable gold monatomic chains suspended between two gold electrodes.[7,8] Stable gold chains have been obtained by stretching gold nanowires. The first-principles calculations for Au by Portal *et al.*[9] showed that finite, as well as infinite, gold atomic wires between two gold electrodes favour the planar zigzag geometry. In a more recent comparative study,[10] Au, Cu, Ca, Al and K infinite chains were found to form planar zigzag structures with the equilateral triangular geometry. Only the Au and Al chain has a second zigzag structure with a wide bond angle $\alpha = 131^\circ$ and 139°,[11] respectively. Note that Au, Cu, Ca and K can all be considered to be similar because of their s-type valence orbitals. On the other hand, aluminium has both s- and p-type valence orbitals, so that it is more complex than those atoms with pure s-type valence electrons. The bonding character has been found to be quite different between aluminium and gold chains.[10,11] Therefore, it is of great importance to understand atomic structures of the 1D systems with more complex valence electronic orbitals (such as Zr atom which has d-type valence electrons), as well as how the electronic properties change in the lower dimensionality.

The density functional theory has been successful in predicting the electronic and structural properties of metals. We present a systematic first-principle analysis of the binding, atomic and electronic structures of very thin Zr chains. The planar structures forming zigzag chains are emphasized. Atomic chains of Au, Cu, Ca, K, and Al as mentioned previously are similar due to their s-type outermost valence orbitals, except that Al has a $3s^2 3p^1$ valency. The situation of Zr, as a transition metal, is expected to be more complex since Zr atom has a $4d^2 4s^2$ valency. The present study shows that the higher the coordination of an individual atom, the stronger is the binding energy. The results also reveal that Zr can form planar chains in zigzag, dimer and ladder structures. The most stable geometry is the zigzag one close to equilateral triangles with four nearest neighbours. Two metastable structures, dimer and ladder, intermediate to distorted linear and triangular structures are also reported. We found that by going from Zr bulk to a Zr chain, the characters of bonding did not change significantly. It is expected that the present analysis will contribute to the understanding of atomic structure and related physical properties of infinite and finite atomic chains.

We have performed *ab initio* pseudopotential total energy calculations within the density-functional theory using the Vienna *ab initio* simulation package (VASP).[12,13] Zr chains are treated within the supercell geometry. In the supercell, the distance between the atomic chains is taken to be 15 Å, which has been tested to be large enough to ignore the inter-chain interactions. The z axis is taken along the chain axis, and y axis (x axis) is perpendicular to (in) the plane of zigzag structure. The wavefunctions are expressed by plane waves with the cutoff energy of $|k + G|^2 \leq 400\,\text{eV}$. The Brillouin-zone (BZ) integration is performed within the Monkhorst–Pack scheme[14] using $(1 \times 1 \times 40)$ $\boldsymbol{k}$-mesh points. The convergence with respect to the energy cutoff and the number of $\boldsymbol{k}$ points has been tested. With larger

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energy cutoff or more $\boldsymbol{k}$ points, the change of total energy of the system is less than 0.01 eV. Ionic potentials are represented by ultrasoft Vanderbilt-type pseudopotential[15,16] and results are obtained by using generalized gradient approximation[17] (GGA) for fully relaxed atomic structures. Preconditioned conjugate gradient method is used for wavefunction optimization. Since ionic relaxations are carried out by the conjugate gradient method the relaxations stop if forces on each atom are less than 0.1 mRy/Å. The external pressure on the supercell is infinitesimal.

The variation of the total energies (E_T) of the Zr atomic chains calculated for the fully relaxed linear, planar zigzag, dimer and ladder structures are shown in Fig. 1. The geometries of these structures and their relevant structural parameters are shown by insets. Since the total energies are given relative to the energy of the free Zr atom, the cohesive energy $E_C = -E_T$. Calculated lattice parameters and cohesive energies of 1D structures as well as the Zr bulk are also listed in Table 1. The zigzag geometry displays two minima: one occurs at $s = 1.43$ Å (parameter s are shown in insets in Fig. 1) and has a cohesive energy $E_c = 6.04$ eV/atom, the other has shallow minimum and occurs at $s = 2.10$ Å with a cohesive energy $E_c = 5.024$ eV/atom. The high cohesive energy zigzag structure (specified as Z_1) has bond length $d = 2.74$ Å and bond angle $\alpha = 63°$ which is quite close to an equilateral triangle of $\alpha = 60°$. The low cohesive energy zigzag structure (specified as Z_2) has a bond length of $d = 2.42$ Å and bond angle $\alpha = 120°$, which allows for only two nearest neighbours. In comparison with the Z_1 structure, we have also calculated the equilateral triangular geometry (specified as T-structure). Results show that T-structure has a slightly larger bond length with $d = 2.78$ Å and slightly lower cohesive energy with $E_c = 6.02$ eV/atom, as compared with Z_1 structure ($d = 2.74$ Å and $E_c = 6.04$ eV/atom). The cohesive energy of the truly linear structure ($\alpha = 180°$, specified as L-structure) is the lowest one (i.e. the most unstable) among the structures studied, with an $E_c = 4.67$ eV/atom. The highest cohesive energy structure (most stable) is the Z_1 structure, with an $E_c = 6.04$ eV/atom which is 1.37 eV/atom higher than that of the L-structure.

Our calculations also show that Zr atomic chain can form a stable dimer structure. The cohesive energy of the dimer chain is $E_c = 4.77$ eV/atom, which is 0.1 eV/atom higher than that of a truly linear chain, L-structure. The dimer bond length is 2.33 Å which is 0.22 Å shorter than that of truly linear chain. Two linear chains can form a ladder structure with $\alpha = 90°$ that allows for three nearest neighbours. The cohesive energy of the ladder structure is $E_c = 5.45$ eV/atom which is in between the Z_1 and Z_2 structures. It is interesting to note that, in the ladder structure, the distance between two linear chains h (2.69 Å) is even slightly shorter than the bond length within the linear chain d (2.73 Å).

Table 1. Calculated lattice parameters and cohesive energies of the 1D and bulk structures for zirconium. The geometric parameters of the structures (s, d, h, α) are explained in Fig. 1.

Structure	s (Å)	d (Å)	α	E_c (eV/atom)
L	2.55	2.55	180°	4.67
Z_1	1.43	2.74	63°	6.04
Z_2	2.10	2.42	120°	5.02
Dimer	2.33	5.43	180°	4.77
Ladder	$h = 2.69$	2.73	180° & 90°	5.45
T	1.39	2.78	60°	6.02
Bulk	$a = b = 3.23$	$c = 5.18$	60° & 90°	8.44

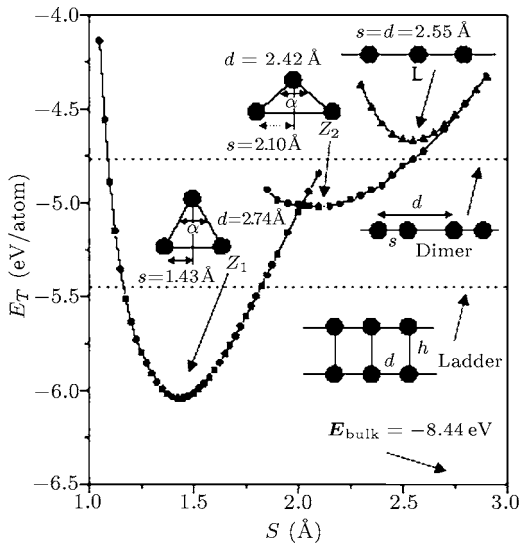

Fig. 1. Calculated total energies E_T (cohesive energy $E_c = -E_T$) of an infinite Zr chain with linear, planar zigzag, dimmer and ladder structures. Energies are given relative to the energy of a free Zr atom. The calculated minimum energies of the dimer and ladder structures are indicated by the dashed lines. Structure parameters, such as bond length d, bond angle α, s and h, are shown by insets. The unit cells of the zigzag structures are shown.

Figure 2 shows the valence charge-density contour plots for Zr bulk, L, Z_1, Z_2, dimer and ladder structures. Similar to the metallic charge density of Zr bulk, there are no obvious directional bonds shown in the figures and valence charges are delocalized in all the 1D structures presently studied. This is quite different from the case of aluminium where the bonding acquires directionality in the one-dimensional structures.[11] Compared the simplest truly linear chain (L-structure) of aluminium and zirconium, it shows that charges are accumulated between atoms forming a directional bond in the Al chain; however, no accumulation of charges between atoms can be seen in the Zr chain. This situation is maintained in all the zigzag (Z_1 and Z_2), dimer and ladder structures of zirconium. We see a metallic distribution of charge density between the doubled atomic chains of the ladder structure. The electron density showed a clear homogenization tendency, with

a net depletion in the interatomic regions in all these one-dimensional structures of Zr. This is also confirmed by the contour plot of charges of an individual bond in a plane perpendicular to the zigzag (xz plane) and passing through the Zr-Zr bond (also shown in Fig. 2). From what is described above, we may find that the charges or bondings of Zr atomic chains are similar to those of Au[9,10] but very different from those of Al.[11] We may therefore expect that stable Zr chains could be obtained by stretching Zr nanowires as in the case of gold.

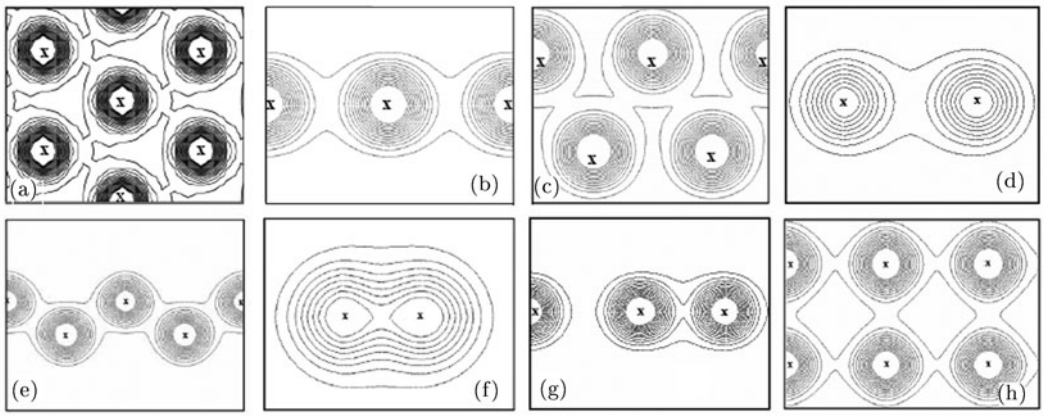

Fig. 2. Valence charge-density contour plots of 3D and 1D Zr structures: (a) bulk; (b) linear L-geometry; (c) Z_1 geometry, on the plane of the zigzag structure (xz plane); (d) Z_1 geometry, on the plane passing through the Zr–Zr bond and perpendicular to the plane of the zigzag structure; (e) Z_2 geometry, on the plane of the zigzag structure (xz plane); (f) Z_2 geometry, on the plane passing through the Zr–Zr bond and perpendicular to the plane of the zigzag structure; (g) dimer geometry; (h) ladder geometry, on the plane of the zigzag structure. Atomic positions are indicated by x.

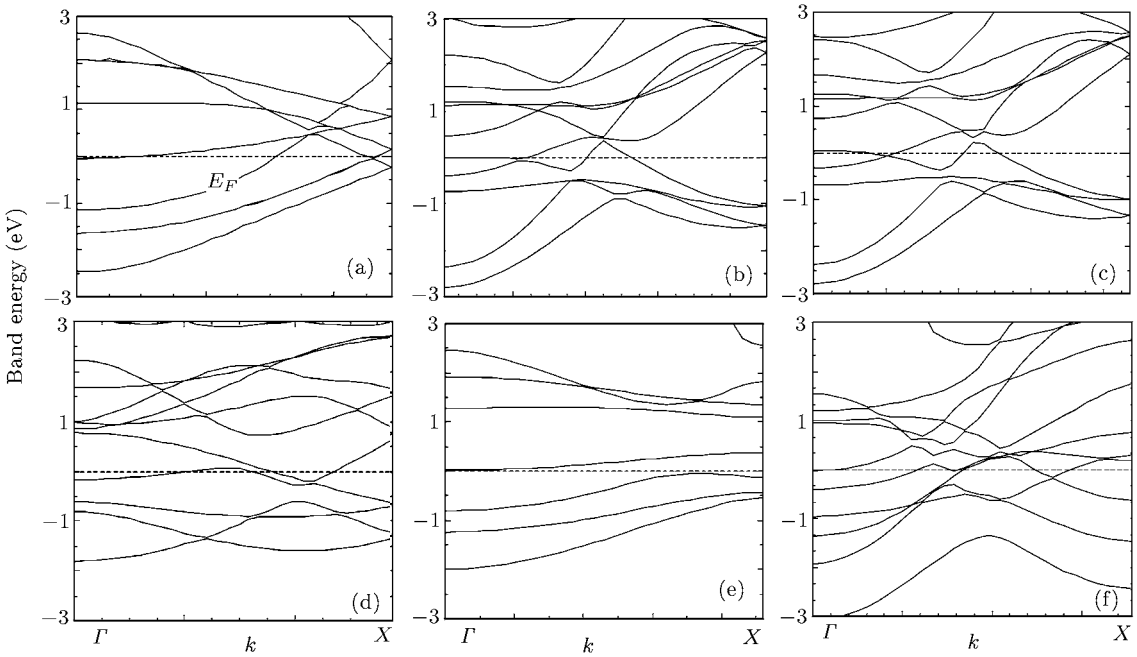

Fig. 3. Energy band structures of Zr chains for (a) linear L-structure; (b) T-structure; (c) zigzag Z_1-structure; (d) zigzag Z_2-structure; (e) dimer structure and (f) ladder structure. Bands of L-structure are folded for the sake of comparison with the other structures. Zero of energy is taken at the Fermi level (dotted lines).

A comparative analysis of the electronic band structures of Zr monatomic chains are illustrated in Fig. 3, which provides a further insight into the stability and the character of bonding. The band structure of the L structure is folded for the sake of comparison with the other structures. The valence electron configuration of a free Zr atom is $4d^2 5s^2$. The band structures of Zr chains are therefore more complicated than the Al chains[11] (with a $3s^2 3p^1$ valency) and K chain (as well as Au, Cu [10] which are all s-type valence orbitals).

Figure 3 shows that the energy band structures of

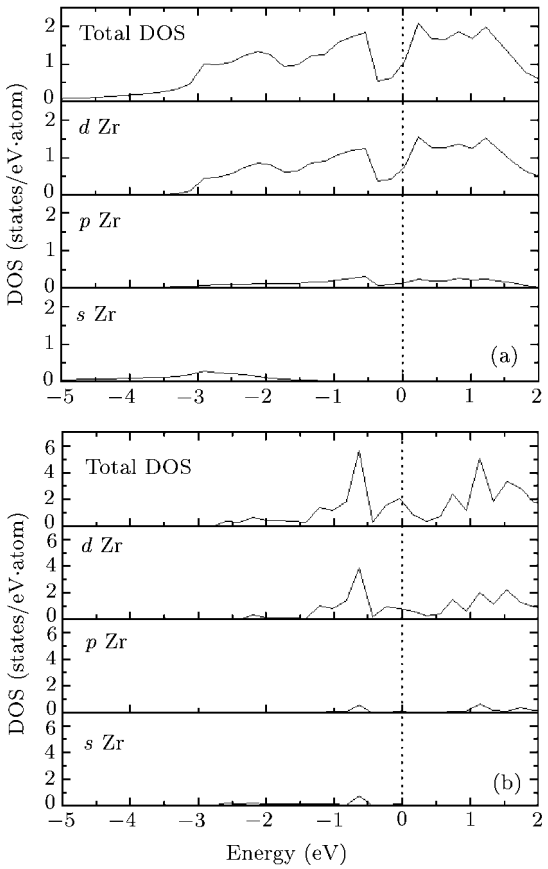

Fig. 4. Electronic density of states (DOS) of Zr for (a) bulk; and (b) Z_1 geometry. Zero of energy is taken at the Fermi level (dotted lines).

Zr chains undergo significant changes in different structures near the Fermi energy. For example, there are four bands crossing the Fermi level in the L-structure (Fig. 3(a)); however, in the dimer structure there are only two flat bands around the Fermi level (Fig. 3(e)), and a more complicated band crossing at the Fermi level is shown in the ladder structure (Fig. 3(f)). Note that flat bands will give a high electronic density of states. The energy bands of T-structure and Z_1-structure (Figs. 3(b) and 3(c)) are rather similar; this is because their geometries are rather close, differing only in the $\alpha = 60°$ and $\alpha = 63°$. In order to understand the relative stability of the two zigzag structures, the electronic density of states (DOS) are also calculated. DOS at the Fermi level is calculated to be 3.78 states/eV/cell for the Z_1-structure and 7.55 states/eV/cell for the Z_2-structure. This significant lowering of the DOS at the Fermi level stabilizes the Z_1-structure relative to the Z_2-structure. In spite of these differences in the band structures, the character of the bonding remains essentially metallic in all the chain structures studied. Figure 4 gives a comparative presentation of the total density of states (TDOS) and partial density of states (PDOS) for both the bulk and the Z_1 structures of zirconium, in order to have a better understand of the Zr–Zr bonding at lower dimension. We also calculate the PDOSs for all the metastable structures as mentioned above. The results show that the density of states at the Fermi level was mainly from the $4d$ electron of Zr atom with a negligible contribution of the s and p electrons of the Zr atom. The DOS at the Fermi level of bulk Zr show a similar character with a slightly larger contribution from p electrons.

As pointed out by Peierls,[18] all the 1D metallic structures with a partly filled band will distort away from a regular chain configuration to lower its energy and lead to band splitting. The energy difference between the dimer structure and the truly 1D chain is calculated to be 0.1 eV/atom, which is the order of magnitude of energy gain due to the Peierls distortion. All the L, Z_1, Z_2, dimer and ladder structures are local minima on the Born–Oppenheimer surface and are expected to be stable at least at low temperatures.

In summary, we have found that a zigzag chain of zirconium close to a triangular configuration is most stable among the planar structures we studied. The structures for planar geometries and bondings are similar to gold. There are no obvious directional bonds in the chains and the valence charges are delocalized. As far as the comparability between zirconium and gold is concerned, zirconium chains have some characters quite similar to gold. Two metastable structures, dimer and ladder, intermediate to linear and triangular structures are also reported. The metallicity of Zr chains has its origin in d bands.

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